Wannier Functions: Localization Properties and Explicit Construction

S. Satpathy and Z. Pawlowska, MPI, Stuttgart (1988)

Look-aikes of Ole and Sashi in the spherical cow approximation

Resurrecting the paper from its grave

Minimal local-orbital sets, direct generation of Wannier-like functions, and applications to HTSCs

**WF**

**Good points:**
- Nice to think about electron states in terms of localized states Cu(d), O(p), etc.
- Local orbitals natural way to build models for correlated systems, e.g., Hubbard models

**Bad points:**
- Not uniquely defined - can vary strongly in shape or range as opposed to Bloch functions that are unique (except for an overall phase factor)

**How to build them:**
- Kohn's variational method
- Superposition of Bloch functions
- NMTO

Implemented by Kane and Kane (1978)
- Too cumbersome

SS+ZP (1988, LMTO), Marzari-Vanderbilt (1997, plane waves)

Choice of phase.

Andersen et al, in progress

**Localization Properties of WF**

Q. How well do we localize the WF?

- People involved: Kohn (1959), Des Cloizeaux (1964), Nenciu (1990)

1 D: For every band, there exists one and only one WF, which has all three of the properties:

1. It is real.
2. It is either symmetric or AS.
3. It falls off exponentially, $W \sim \exp(\cdot\cdot\cdot)$. Related to the analyticity of the band structure in the complex $k$ space

Decay constant $A$ is related to how far away is the branch point in the complex $k$ plane.

$$A \sim \frac{\text{Gap}}{1/2}$$

If Bloch functions $\psi_k(x)$ are differentiable in $k$ and analytic in a complex neighborhood of $k$, then the WF falls off exponentially. (Nenciu, RMP, 1991)

Q. Can one construct more localized function by relaxing reality and symmetry conditions?

Answer: NO!

For touching bands, there is no exponential localization!!
Localization of WF in 3D

- Isolated single band
  
  exponential localization is proved. (Nenciu, Commun. Math. 
  Phys., 91, 81 (1983))

- Multiple bands (Des Cloizeaux, PR 135, A698 (1964))
  
  in “many” cases, it can be proved that:

  If Bloch functions are analytic in the domain of
K = K' + iK'' for |K''| < A, then the
  corresponding WF falls off exponentially.

  Working conjecture: For all cases of isolated groups of
bands, exponentially localized WF exists, but no proof for
  existence has not been found yet!
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Calculation Details

- With that conjecture, we proceed to compute WF for a 3D composite bands.
  (valence bands of Si)
- Stick to the established ideas in 1D
  a) Reality of \( \gamma_k \)
  b) Symmetry (maximum symmetry compatible with 3D bands)
  (\( \Gamma \) irrep of \( D_3d \) group)
- Compute \( \gamma_k \) using LMTO in the \( \frac{1}{4} \)th BZ and construct \( \gamma_k \) in full zone
  from symmetry
- Choice of phase factor: \( e^{-i\kappa_r} \)
  \( \langle \gamma_k | \psi \rangle = \sum_{m=1}^{N} U(x) \langle \gamma_m | \psi \rangle e^{-i\kappa_r} \)

**Sp\(^3\) Bond orbital (BO)**

- Directed bond: \( \frac{1}{2}(s+x+y+z) \)
- \( \text{BO} = \frac{1}{\sqrt{2}} (b_1 + b_2) \)

**The four sp\(^3\) Bond orbitals span the same symmetry as the four valence bands at every \( k \) point in the Brillouin zone**

WF will have to have the same symmetry as that of the sp\(^3\) bond orbital, viz., the \( \Gamma_1 \) irrep of the \( D_3d \) (tetrahedral) group.

Else, stuff such as degeneracies etc. will not be correct for bands obtained with the WF of wrong symmetry.

"continuity chord" ideas: see J. Zak, PRL 54, 1075 (1985)
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**sp³ bond orbital character dominates in the valence charge density of Group-IV semiconductors**

- Bond orbital 72% for Si, while AB is just 4%.
- “Bond-order” (B-AB) progressively weakens in going from C to a-Sn.
- Quantitative justification for focusing on the sp³ BO part in constructing the WF.

<table>
<thead>
<tr>
<th>crystal</th>
<th>lattice constant (Å)</th>
<th>character (%)</th>
<th>Si-Si 3</th>
<th>Si-Si AB</th>
<th>Si-d</th>
<th>Ex. 2, 4</th>
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<tbody>
<tr>
<td>C</td>
<td>0.356</td>
<td>77</td>
<td>1</td>
<td>3</td>
<td>19</td>
<td></td>
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<tr>
<td>Si</td>
<td>0.540</td>
<td>77</td>
<td>4</td>
<td>8</td>
<td>20</td>
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<tr>
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<td>77</td>
<td>5</td>
<td>8</td>
<td>20</td>
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<tr>
<td>w-Sn</td>
<td>0.549</td>
<td>71</td>
<td>6</td>
<td>8</td>
<td>20</td>
<td></td>
</tr>
</tbody>
</table>

*Construct WF such that the projection of it to the central BO is maximized.

**Test of convergence of log |Ψ(cell)|² as a function of the number of k points**
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**Wannier Function for Silicon**

WF constructed with LMTO (SS+ZP, 1988)

**Charge-density character of the WF**

<table>
<thead>
<tr>
<th>cell location</th>
<th>silicon</th>
<th>empty sphere</th>
<th>total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>central</td>
<td>rest</td>
<td>d</td>
</tr>
<tr>
<td>central cell</td>
<td>sp$^3$ bond</td>
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<td>2</td>
</tr>
<tr>
<td>nearest-neighbor cell</td>
<td>sp$^3$ anti-bond</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>rest</td>
<td>18</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>total</td>
<td>54</td>
<td>0</td>
<td>22</td>
</tr>
</tbody>
</table>

Character of the silicon charge-density for C, Si, Ge, and α-Sn

<table>
<thead>
<tr>
<th>crystal</th>
<th>lattice constant (nm)</th>
<th>character (%)</th>
<th>B</th>
<th>B-Sn AB</th>
<th>BS-d</th>
<th>E-d</th>
<th>E-d, p, d</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.356</td>
<td>77</td>
<td>1</td>
<td>3</td>
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<td></td>
<td></td>
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<tr>
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<tr>
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<tr>
<td>α-Sn</td>
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<td>71</td>
<td>5</td>
<td>4</td>
<td>29</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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Exponential localization of the calculated WF

Complex band structure of Chang using empirical TB (PRB, 25, 605 (1982)).
Branch-points of $E(k)$ at $k$$\frac{\pi}{a}$$7$$\pi/a_{k_{111}}$, and $k$$\frac{\pi}{a}$$5$$\pi/a_{k_{100}}$.

If we assume no other branch point in the range $|\text{Im}(K)|<0.5\pi/a$, then that indicates a decay of $W \sim \exp(-d/0.64a)$.

[log $|\Psi_{\text{cell}}|^2$ vs. distance of cell from origin d (units of lattice constant), showing exponential decay. SS and ZP (1988)]
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**Wannier Function for Silicon**

So-called “Maximally projected” WF constructed with LMTO (to maximize BO contribution) (SS+ZP, 1988)

So-called “Maximally localized” WF constructed with plane-wave pseudopotential (Marzari & Vanderbilt, 1997)

Test of convergence of $\log |\Psi_{\text{cell}}|^2$ as a function of the number of k points (SS+ZP)

$N = \# \text{ of k points in } \frac{1}{48} \text{th BZ}$
Integrated charge-density character of the WF, $S(d)$, within a sphere of radius '$d$'.

Conclusion

- Bond-centered WF constructed for the Si valence bands, by direct superposition of Bloch functions and a choice of phase to maximize the sp$^3$ BO contribution.
- Exponential fall off of the WF demonstrated: $W \sim \exp(-d/0.8\ a)$
- This is the most localized in the sense that the central sp$^3$ character is maximum; this character will necessarily reduce if we maximize some local operator, such as $\langle W|1/r^2|W\rangle$, instead.
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Issues and Questions

- Uniqueness
- How universal is the method for calculating WF?
- NMTO as a method to compute WF
- How to compute parameters (U etc) for model Hamiltonians in some unique manner?
- WF for non-isolated bands - How crucial is the lack of exponential localization?